

AD-A041 866 PENNSYLVANIA UNIV PHILADELPHIA LAB FOR RESEARCH ON --ETC F/G 7/3
SYNTHESIS OF ELECTRICALLY-CONDUCTING ORGANIC POLYMERS: HALOGEN --ETC(U)
JUL 77 H SHIRAKAWA, E J LOUIS, A G MACDIARMID N00014-75-C-0962
UNCLASSIFIED LRSM-TR-77-1 NL

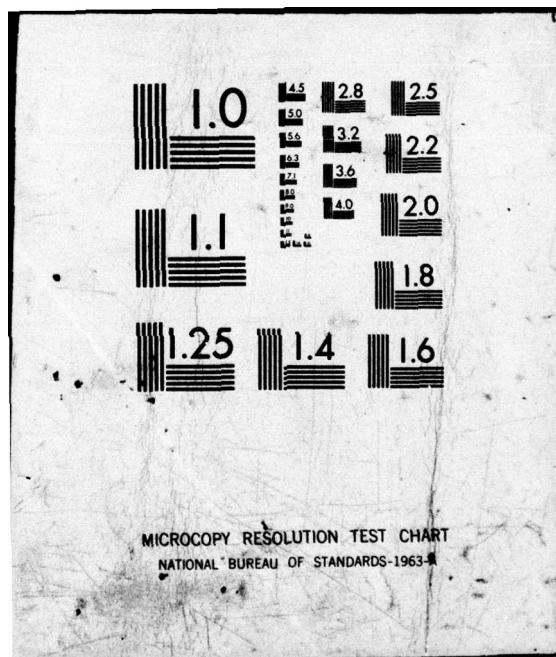
1 OF 1
ADA041 866



END

DATE
FILMED
8-77





Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ADA041866

REPORT DOCUMENTATION PAGE			READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACQUISITION NO.	3. REPORTER'S CATALOG NUMBER	12
Technical Report No. 77-1			9
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED		
Synthesis of Electrically-Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH) _x	Interim Technical Report		
6. PERFORMING ORG. REPORT NUMBER			
7. AUTHOR(S)	8. CONTRACT OR GRANT NUMBER(S)		
Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid, Chwan K. Chiang and Alan J. Heeger	N00014-75-C-0962		
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS		
Departments of Chemistry and Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19104	NR-356-602 14 Jul 77		
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE		
Department of the Navy Office of Naval Research Arlington, Virginia 22217	July 14, 1977		
13. NUMBER OF PAGES	14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		
Nine	14) LRSM-TR-77-1		
15. SECURITY CLASS. (of this report)	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
Unclassified	DDC RECEIVED JUL 19 1977 C		
16. DISTRIBUTION STATEMENT (of this Report)	17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
Distribution unlimited; approved for public release.			
18. SUPPLEMENTARY NOTES			
Accepted for publication in J.C.S., Chemical Communications.			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
Silvery films, semiconducting-polymer, trans "polyacetylene," (CH) _x , conductivity, halogenation, covalent organic polymer, conjugated polyene, acetylene, Ziegler catalyst, electronic properties, (CHBr) _x , halogen-doped material, four probe dc techniques, (CHBr _{0.05}) _x , (CHBr _{0.23}) _x , (CHI _{0.22}) _x , (CHI _{0.05}) _x , charge transfer complexes, carbonium ion complexes, metallic behavior.			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
When silvery films of the semiconducting polymer, trans "polyacetylene," (CH) _x , are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs, and the electrical conductivity increases markedly (over seven orders of magnitude in the case of iodine) to give, depending on the extent of halogenation, silvery or silvery-black films, some of which have a remarkably high conductivity at room temperature.			

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0962

Task No. 356-602

TECHNICAL REPORT NO. 77-1

Synthesis of Electrically-Conducting Organic
Polymers: Halogen Derivatives of Polyacetylene, $(CH)_x$

by

Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid,
Chwan K. Chiang[†] and Alan J. Heeger[†]

Prepared for Publication

in the

J.C.S., Chemical Communications

Department of Chemistry and
Department of Physics,
→ Laboratory for Research on the Structure of Matter,
University of Pennsylvania,
Philadelphia, PA 19104

July 14, 1977

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for public release; distribution unlimited.

ACCESSION FOR	
NTIS	White Section <input checked="" type="checkbox"/>
DOC	Buff Section <input type="checkbox"/>
UNANNOUNCED <input type="checkbox"/>	
JUSTIFICATION.....	
.....	
BY.....	
DISTRIBUTION/AVAILABILITY CODES	
DTG.	AVAIL. AND/OR SPECIAL
A	

Synthesis of Electrically-Conducting Organic Polymers:

Halogen Derivatives of Polyacetylene, $(CH)_x$

By Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid, *
Chwan K. Chiang, + and Alan J. Heeger +

(Department of Chemistry and + Department of Physics,

Laboratory for Research on the Structure of Matter

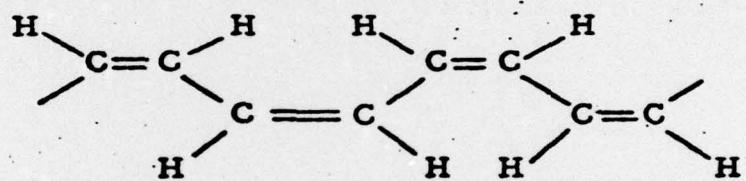
University of Pennsylvania, Philadelphia, PA 19104

Summary - When silvery films of the semiconducting polymer, trans "polyacetylene", $(CH)_x$, are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs, and the conductivity increases markedly (over seven orders of magnitude in the case of iodine) to give, depending on the extent of halogenation, silvery or silvery-black films, some of which have a remarkably high conductivity at room temperature.

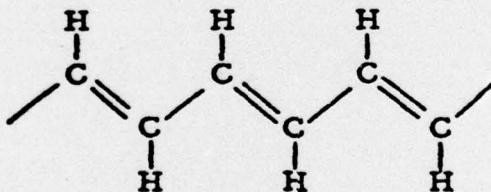
Considerable interest has recently been shown in the synthesis

and study of metallic covalent polymers such as $(SN)_x^1$ and $(SNBr)_y^2$.

In attempting to find a covalent organic polymer which would be a metal or at least have a high conductivity, we have focused our attention on the simplest organic polymer, "polyacetylene", $(CH)_x$. In a series of studies, Shirakawa et al. ³⁻⁷ have succeeded in synthesizing high quality flexible copper-colored films of the cis isomer



and silvery films of the trans isomer



of this conjugated polyene from acetylene in the presence of a

Zeigler catalyst, and they have developed techniques for controlling the

cis and trans content. ^{5, 6} X-ray diffraction and scanning electron

micrograph studies show that films of any cis and trans composition

are crystalline and consist of matted fibrils. ⁵ These materials are

semiconductors; ⁷ the trans isomer, which is the thermodynamically stable

form at room temperature, has a higher conductivity ($\sigma_{273\text{ K}} = 4.4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$) than the cis isomer ($\sigma_{273\text{ K}} = 1.7 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$). ⁷

Shirakawa and Ikeda⁸ have noted that when $(CH)_x$ films are exposed to bromine or chlorine vapor at room temperature for a few minutes, a dramatic decrease in infrared transmission ($4,000 \text{ cm.}^{-1}$ to 400 cm.^{-1}) occurs without any visible change in appearance of the films. Complete halogenation to yield, e.g. $(CHBr)_x$, results again in high infrared transmission with concomitant production of a white film. The initial reduction in infrared transmission suggests that the halogen-doped material might have unusual electronic properties. The results of studies involving the halogenation of films of trans-($CH)_x are summarized below.$

The conductivity of the $(CH)_x$ films were measured by four probe dc techniques at room temperature in a glass vessel to which was attached a bulb containing the halogen. This bulb was held at various temperatures to produce known halogen vapor pressures. When $(CH)_x$ is exposed to 1 Torr of bromine vapor at room temperature for 10 min. the conductivity rapidly increases by approximately four orders of magnitude to give silvery films of $(CHBr_{0.05})_x$ having a conductivity of $0.5 \text{ ohm}^{-1} \text{ cm.}^{-1}$ at room temperature. Longer bromination gives silvery-black films having the composition $(CHBr_{0.23})_x$ and a slightly smaller conductivity ($\sigma_{298 \text{ K}} = 0.4 \text{ ohm}^{-1} \text{ cm.}^{-1}$). The films are stable both in vacuum and when exposed to air for at least several hours at room temperature. Qualitatively similar results are obtained with chlorine, but the increase in conductivity is smaller (about three orders of magnitude).

When iodine vapor reacts with $(CH)_x$ at room temperature, the infrared transmission decreases in a manner similar to that described above for bromine. However, the increase in conductivity is even more remarkable, over seven orders of magnitude, as shown in Figure 1. The maximum conductivity ($\sigma_{298\text{ K}} = 38 \text{ ohm}^{-1} \text{ cm.}^{-1}$) was observed on a silvery-black film of composition $(CHI_{0.22})_x^*$. The appearance of the $(CH)_x$ film remained essentially unchanged until the approximate composition $(CHI_{0.05})_x$ was reached, after which it began to darken. The stability of the iodinated films is similar to that of the brominated material. Separate measurements of three samples of $(CHI_{0.22})_x$ gave an average conductivity of $30 \text{ ohm}^{-1} \text{ cm.}^{-1}$. This material has the largest room temperature conductivity observed for any covalent organic polymer.

We believe that charge-transfer complexes are formed between $(CH)_x$ and halogens when they are permitted to react under certain conditions, as has been observed previously with iodine and polyphenylene.⁹ However, in the case of $(CH)_x$ the absolute conductivities obtained are four to five orders of magnitude greater.

The highly conducting polyacetylene bromides and iodides may be charge-transfer pi complexes of the type believed to be formed during the halogenation of olefins. Stable colored compounds which may be charge-transfer and/or carbonium ion complexes of this type have been obtained by the action of bromine on certain substituted ethylenes.¹⁰

* Analytical data (Galbraith Laboratories, Inc. Knoxville, Tenn. 37921):
 Calcd. for $(CHI_{0.22})_x$, C, 29.34; H, 2.46; I, 68.20. Found: C, 29.14;
 H, 2.62; I, 68.20%. (Total = 100.02%).

We note for comparison that the room temperature conductivity of a compacted, polycrystalline pellet of the organic charge transfer metallic salt, (TTF)(TCNQ) is ca. $10 \text{ ohm}^{-1} \text{ cm.}^{-1}$, ¹¹ while that of a compressed pellet of polycrystalline $(\text{SN})_x$ at room temperature is ca. $20 \text{ ohm}^{-1} \text{ cm.}^{-1}$. ¹² The conductivity of the latter material decreases on lowering the temperature and exhibits an activation energy, E_a , of about 0.02 eV. Later experimental results on single crystals of $(\text{SN})_x$ have shown that the conductivity increases with decrease in temperature, ($E_a = 0$), in a manner characteristic of a metal. ¹ In the polycrystalline $(\text{SN})_x$ sample, the increase in conductivity on lowering the temperature which occurs within a small, metallic crystal of $(\text{SN})_x$ is apparently more than off-set by the decrease in conductivity involved in the passage of electrons from one crystal to another. Like polycrystalline $(\text{SN})_x$, the conductivity of the most highly conducting composition, $(\text{CHI}_{0.22})_x$, decreases slowly on decreasing the temperature ($300 \text{ K} > T > 4.2 \text{ K}$) with an activation energy, $E_a \approx 0.016 \text{ eV}$ (for comparison the activation energy for trans-(CH)_x is $E_a \approx 0.3 \text{ eV}$ ⁷). These results are suggestive of metallic behavior; experiments are underway directed toward clarification of the origin of the very small activation energy.

Although the randomness of the halogenated polyacetylene may be playing an important role, the overall behavior is like that of a series of semiconductors with activation energies which vary with halogen

content. However, a detailed study of the temperature dependence of the conductivity indicates that a simple semiconductor model involving a single activation energy is inadequate to describe the conductivity of the material. We believe the polyacetylene halides may be the for-runners of a new class of organic polymers with electrical properties which may be systematically and controllably varied over a wide range by chemical doping.

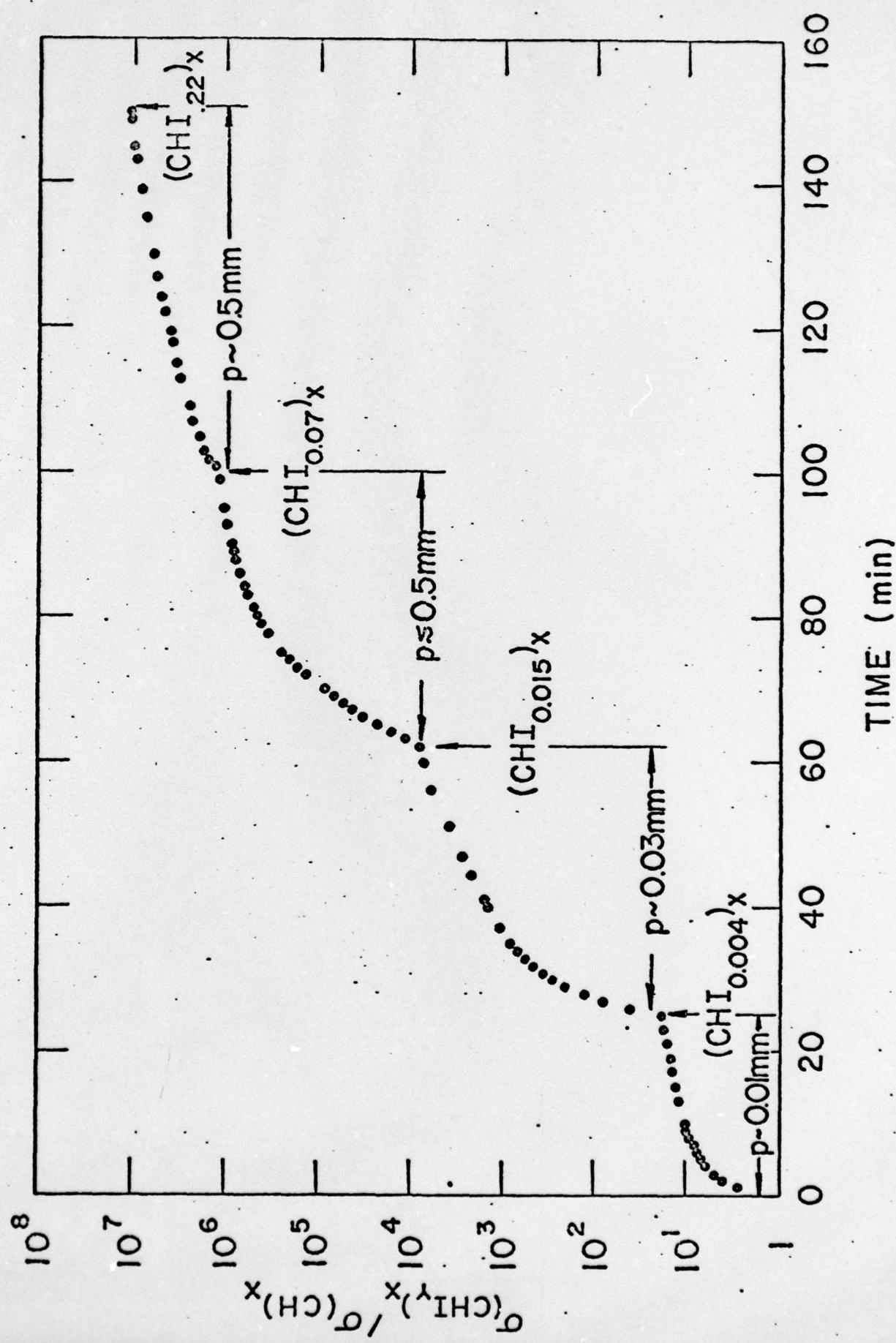
Acknowledgement: This work was supported by the Office of Naval Research Contract No. N00014-75-C-0962.

References:

1. See, for example, V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, Phys. Rev. Lett. 31, 1139 (1973); C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito and A. J. Heeger, J. Amer. Chem. Soc. 97, 6358 (1975); R. L. Greene, G. B. Street, and L. J. Suter, Phys. Rev. Lett. 34, 577 (1975); R. H. Baughman, P. A. Apgar, R. R. Chance, A. G. MacDiarmid and A. F. Garito, J. Chem. Phys. 66, 401 (1977); H. P. Geserich and L. Pintschovius, in Festkorperprobleme (Advances in Solid State Physics), Vol. XVI, p. 65, J. Treusch (ed.) Vieweg, Braunschweig (1976).
2. M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, M. J. Moran, C. K. Chiang, M. J. Cohen, A. J. Heeger and D. L. Peebles, Chem. Commun. in press (1977); G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene and J. J. Mayerle, Chem. Commun. in press (1977).
3. H. Shirakawa and S. Ikeda, Polym. J. 2, 231 (1971).
4. H. Shirakawa, T. Ito and S. Ikeda, Polym. J. 4, 460 (1973).
5. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed., 12, 11 (1974).
6. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. 13, 1943 (1975).
7. H. Shirakawa, T. Ito and S. Ikeda, (unpublished results) (1976).
8. H. Shirakawa and S. Ikeda, (unpublished results) (1976).
9. S. B. Mainthia, P. L. Kronick, H. U. E. F. Chapman and M. M. Labes, Polym. prepr. Amer. Chem. Soc., Div. Polym. Chem. 4, No. 1, April (1963).
10. R. E. Buckles and N. A. Meinhardt, J. Amer. Chem. Soc. 74, 1171 (1952); R. E. Buckles and W. D. Womer, J. Amer. Chem. Soc. 80, 5058 (1958).
11. L. B. Coleman, Ph. D. Thesis, University of Pennsylvania, (1975).
12. M. M. Labes, Pure Appl. Chem. 12, 275 (1966).

Figure Caption:

Figure 1: Increase in the room temperature conductivity of trans-polyacetylene, $(CH)_x$, as a function of time at fixed iodine vapor pressures. The initial room temperature conductivity is 3.2×10^{-5} (ohm-cm) $^{-1}$. [In the last experiment some iodine was sublimed onto the glass walls of the conductivity apparatus in order to promote attainment of the equilibrium vapor pressure of the iodine at room temperature in the vicinity of the film.]



TECHNICAL REPORT DISTRIBUTION LIST

<u>No. Copies</u>	<u>No. Copies</u>		
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6	U.S. Army Research Office P.O. Box 12211 Research Triangle Park, North Carolina 27709 Attn: CRD-AA-IP	
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Library, Code 2029 (ONRL)	6	Prof. Lydia M. Fenzel University of New Orleans Department of Chemistry New Orleans, Louisiana 70122	
Technical Info. Div. Code 6100, 6170	1		
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1		

TECHNICAL REPORT DISTRIBUTION LIST

<u>No. Copies</u>	<u>No. Copies</u>		
Dr. T. C. Williams Union Carbide Corp. Chemicals & Plastics Tarrytown Technical Center Tarrytown, New York 10591	1	Dr. M. Good Department of Chemistry University of New Orleans Lakefront New Orleans, Louisiana 70122	1
Dr. K. A. Reynard Horizons Inc. 23800 Mercantile Road Cleveland, Ohio 44122	1	Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library C1 290/36-84 AUTO-Sutton	1
Dr. R. Soulen, Director Contract Research Department Pennwalt Corp. 900 First Avenue King of Prussia, Pennsylvania 19406	1	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 19-1	
Dr. A. C. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1	Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1
Dr. E. Hedaya Union Carbide Corp. Corporate Research Laboratory Tarrytown, Technical Center Tarrytown, New York 10591	1	Dr. G. Goodman Globe-Union Inc. 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. A. Rheingold SUNY Plattsburgh Department of Chemistry Plattsburgh, New York 12901	1	Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	
Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1	Dr. Martin H. Kaufman, Head Materials Research Branch (Code 15-2) Naval Weapons Center China Lake, California 93555	
Dr. H. Allcock Pennsylvania State University University Park, Pennsylvania 16802	1		
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106			
Dr. R. Lenz Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1		